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AN ANALYSIS OF THE VISIBLE CHEMILU-MINESCENCE OBSERVED IN THE GAS-PHASE OXIDATION OF ALUMINUM AND ITS COMPOUNDS

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Aerodyne Research, Incorporated

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A mechanism based on the population of and emission from the $(A^2\Pi)$ and/or lowest lying $^4\Sigma^+$ and $^4\Pi$ states of AlO is suggested as an explanation for the visible chemiluminescence often observed in the gas-phase oxidation of aluminum. Data from upper atmospheric chemical release experiments utilizing aluminized grenades, aluminized burners, and trimethylaluminum are examined, and AlO* pumping steps based on the reaction of molecules containing loosely bound aluminum atoms with atomic oxygen are suggested. Previously proposed theories

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are shown to be unable to reproduce reasonably the observed data.

The results of selected, recent laboratory experiments involving chemiluminescent reactions of metal atoms and dimers with electrophilic atoms and molecules are discussed in terms of the proposed mechanism. Several possible experiments to test the proposed mechanism are suggested.

AN ANALYSIS OF THE VISIBLE CHEMILUMINESCENCE
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ii

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TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

INTRODUCTION

An intense, visible chemiluminescence is often observed during the gas-phase oxidation of aluminum or aluminum containing compounds. This chemiluminescence is usually dominated by a broad "continuum," which peaks between 500 and 620 nm, and often remains above half-peak power at 400 and 750 nm. A short-wavelength cutoff near 350 nm is evident.

Laboratory observations of this chemiluminescence continuum have been reported in the reaction of atomic oxygen with aluminum vapor[1] and trimethylaluminum (TMA),[1,2,3] in premixed TMA/O_2 flames,[4] in the reaction of TMA with O_2 (a $^1\Delta$),[5] in the interaction of molecular beams of aluminum vapor and ozone,[6] in laser-supported detonation waves in air on aluminum surfaces,[7] and possibly in the oxidation of exploding aluminum wires.[8] However, the most dramatic observations of this aluminum-oxygen continuum involve the interaction of the gaseous products from either aluminum loaded grenades,[9-13] or from the oxidation of TMA,[14] with the upper atmosphere between 90 and 220 km in altitude. The purpose of this paper is to examine the molecular mechanism responsible for this chemiluminescence.

CHARACTERISTICS OF UPPER ATMOSPHERIC ALUMINUM GLOWS

The visible chemiluminescent glows from aluminum containing upper atmospheric releases are strong enough and persistent enough that characteristic upper atmospheric diffusion coefficients have been derived from observations of the rate of growth of these chemiluminescent "clouds."[15-17] However, this technique has been superseded by twilight releases into the sunlit upper atmosphere. These result in the superimposition of the strong, solar-pumped fluorescence of the AlO ($B\,^2\Sigma^+ - X\,^2\Sigma^+$) transition on top of the chemiluminescence, thereby producing a brighter and longer-lived cloud.[15-19]

The wavelength dependence of the chemiluminescent glows from aluminized grenade and TMA upper atmospheric releases is sufficiently similar that it has long been assumed that both glows arise from the same emitting species.[14] This assumption is strengthened by the fact that a major chemical component of both types of release clouds is AlO, a fact demonstrated by the solar-induced fluorescent emission from the AlO ($B \rightarrow X$) band.[20] Application of the recent determination of the AlO ($B \rightarrow X$) transition f number[21] to quantitative measurements of the steady-state AlO concentration produced by TMA clouds at altitudes from 125 to 162 km[22] indicates that at least one to eight percent of the aluminum released as TMA is present as AlO for times on the order of several minutes.

Data on the total radiant intensity of both aluminized grenade and TMA clouds indicate that the light producing reaction is very efficient. Accurate quantum yields are difficult to deduce both because the total radiant intensity measurements suffer from instrumentation and interpretation difficulties and because the molecular distribution of released products is not well-known. (Only equilibrium calculations of exploding grenade products are available. Also, TMA is released as a liquid, part of which flash vaporizes to a dimer/monomer mixture while the rest freezes and may or may not participate in the glow producing reaction. However, published measurements of total radiant intensities indicate that the yield of "continuum", visible photons may be as high as 0.6 per molecule of vaporized aluminum containing molecules.[10,13,14] The quantum yield for grenade releases rises sharply between 95 and 120 km, and plateaus or drops slightly above that altitude.[13] Similar data for TMA releases have not been published. 2

PREVIOUSLY SUGGESTED CHEMILUMINESCENT MECHANISMS

The actual molecular identity of the chemiluminescent species has not yet been experimentally determined in either laboratory or upper atmospheric studies. However, strong evidence that the emitting species contains aluminum is contained in the observation that purely organic explosive grenades containing aluminum granules produce the characteristic glows at 114 km, while the same grenades without aluminum do not.[10] The conclusion that the emitting species is an aluminum oxide is drawn not only from the various laboratory studies with controlled oxidizing environments,[1-8] but also from the observation that atmospheric releases do not produce this characteristic radiation at altitudes below the onset of atomic oxygen as a significant atmospheric component.[13]

Rosenberg, et al.,[10] have suggested the most widely quoted mechanism for the aluminum-oxygen chemiluminescent continuum. This mechanism is analogous to the well-known nitric oxide, oxygen atom recombination continuum, and is presented in Eqs. (1) - (4):

$$AlO + O \rightarrow AlO_2^* \tag{1}$$

$$AlO_2^* + M \rightarrow AlO_2 + M \tag{2}$$

$$AlO_2^* \rightarrow AlO_2 + h\nu \tag{3}$$

$$AlO_2 + O \rightarrow AlO + O_2 \quad , \tag{4}$$

where (*) denotes an electronically excited molecule. Rosenberg's mechanism is attractive from the standpoint that it involves only reactants which are known to be present in the release cloud (AlO is detected by solar-pumped fluorescence and atomic oxygen is a well-known atmospheric constituent at altitudes above 85 km). In addition, reaction (4), which regenerates AlO, allows a chain process, which is always helpful in accounting for high chemiluminescent quantum yields.

3

However, the mechanism shown in reactions (1) - (4) runs into serious difficulty when applied to quantitative observations. In fitting this reaction scheme to their observations of grenade releases, Johnson and co-workers[13] discovered that they would need an effective radiative recombination rate constant k_5 for the combination of reactions (1) and (3) (ignoring the quenching reaction (2)) of 1×10^{-13} cm^3/sec.

$$AlO + O \xrightarrow{k_5} AlO_2 + h\nu \tag{5}$$

The chemiluminous glows from nighttime trimethyaluminum release can also be analyzed to yield an estimate of the magnitude of k_5 necessary for the AlO + O radiative recombination mechanism to explain the data. Rosenberg, et al., have characterized their TMA clouds as emitting 10^{-2} photons per second per TMA molecule released at 100 km, and 10^{-3} photons per second per TMA molecule released at 160 km.[24]

Thus, the average photon emission per cubic centimeter from the 100 km cloud can be written

$$\frac{d\overline{(h\nu)}}{dt} = \frac{\alpha N_{TMA}}{V} \quad , \tag{6}$$

where N_{TMA} is the number of TMA molecules released, V is the cloud volume in cubic centimeters, and α is the number of photons per second per TMA molecule released. However, if the emission is due to reaction (5), the photon emission per unit volume can also be written

$$\frac{d\overline{(h\nu)}}{dt} = k_5 \left[AlO\right]\left[O\right] \quad , \tag{7}$$

where $\left[AlO\right]$ and $\left[O\right]$ are the average species concentrations in the cloud. The unperturbed atomic oxygen concentrations for 100 and 160 km are near 1.09×10^{12} and 1.66×10^{10} atoms/cm^3, respectively.[23] It should be noted that substitution of the unperturbed atomic oxygen content into Eq. (7) will produce a conservative lower estimate for k_5, since the real atomic oxygen content in the cloud will be reduced

4

from the unperturbed value by reaction with TMA and its oxidation products. The AlO concentration in the glowing cloud can b related to N_{TMA} by utilizing the previously mentioned twilight solar fluorescence measurements.[22] As noted previously, correction of the published ratios by utilizing the recent, direct laboratory measurement of the AlO (B $\rightarrow$ X) f number[21] yields an estimate of the total AlO cloud content as 0.08 N_{TMA} at 162 km, decreasing to 0.01 N_{TMA} at 120 km. Thus, 0.1 N_{TMA} is a conservatively large estimate of total cloud AlO at altitudes between 100 and 160 km. This leads to an estimate of the average AlO concentration per unit volume of 0.1 N_{TMA}/V. Using the values of $\left[O\right]$ and $\left[AlO\right]$ discussed above, Eq. (7) can be rewritten as

$$\frac{d\,\overline{(h\nu)}}{dt} \approx k_5\,\frac{0.1\,N_{TMA}}{V}\,\left[O\right] \quad ; \tag{8}$$

equating Eq. (8) and Eq. (6) yields

$$\frac{\alpha\,N_{TMA}}{V} \approx k_5\,\frac{0.1\,N_{TMA}}{V}\,\left[O\right] \quad . \tag{9}$$

and rearrangement yields

$$k_5 \approx \frac{\alpha}{0.1}\quad\frac{1}{\left[O\right]} \quad . \tag{10}$$

Utilizing the estimated values of α and $\left[O\right]$ for 100 km yields an estimate,

$$k_5 \approx \frac{0.01}{0.1}\quad\frac{1}{1.09 \times 10^{12}} \approx 0.92 \times 10^{-13}\,cm^3/sec \quad . \tag{11}$$

Substituting α and $\left[O\right]$ values for 160 km yields

$$k_5 \approx \frac{0.001}{0.1}\quad\frac{1}{1.66 \times 10^{10}} \approx 6.0 \times 10^{-13}\,cm^3/sec \quad . \tag{12}$$

5

These estimates of k_5 are comparable to the 1×10^{-13} cm^3/sec value derived by Johnson, et al., from their grenade produced glow data. Lower average concentrations of either aluminum monoxide or atomic oxygen in the clouds would, of course, produce even larger estimates of k_5.

It is quite unreasonable to expect reaction (5) to proceed with a rate constant anywhere near as large as 1 to 6×10^{-13} cm^3/sec. Radiative recombination rate constants for two or three atom systems seldom exceed 10^{-16} cm^3/sec, even in their high pressure "effective biomolecular" limits. For example, at typical atmospheric densities ($< 10^{12}$ molecules/cm^3) and temperatures (300~500°K) characteristic of 120 km[23] (where the grenade-produced aluminum oxide chemiluminescence plateaus), the well-known NO + O "air afterflow" reaction exhibits a biomolecular rate of 1×10^{-17} to 5×10^{-18} cm^3/sec.[25] Since the O + NO radiative recombination, which is one of the most facile reactions of this type known, proceeds at a rate more than 10^4 times slower under upper atmospheric conditions than needed for AlO + O, it seems unreasonable to ascribe the aluminum oxide chemiluminescence to reaction (5).

Schiff has suggested that the chemiluminescence created in the interaction of atomic oxygen with the dimeric form of trimethylaluminum may be due to the reaction

$$\left[Al\,(CH_3)_3 \right]_2 + O \rightarrow Al_2O^* + 6\,CH_3 \quad , \tag{13}$$

which he stated to be more than 50 kcal/mole exothermic.[1] However, the average Al-CH$_3$ bond strength in trimethylaluminum has been measured as 64.5[26] or 62.9[27] kcal/mole, and either of these values, coupled with the dimer dissociation energy of 20.2 kcal/mole[26] and the Al$_2$O atomization energy of 249 kcal/mole[28] makes reaction (13) more than 140 kcal/mole endothermic. Thus, reaction (13) can be ruled out as the mechanism responsible for the chemiluminescence observed in TMA oxidation.

AlO* PROPOSED AS CONTINUUM EMITTER

Previously proposed chemiluminescent reaction mechanisms leading to the aluminum oxide "continuum" have focused on triatomic emitters such as AlO_2 or Al_2O because it is widely assumed that a diatomic molecule such as AlO cannot produce a wide-band, continuum-like spectrum. However, recent laboratory investigations of gas-phase, exothermic, metal-oxidizer reactions have led to the identification of very broad band emissions from chemically pumped states of metal-oxide or metal-halogen diatomics. Under low resolution, such visible emissions can appear to be "continuum" over a range of several thousand angstroms in wavelength. The published laboratory and upper atmospheric observations of the aluminum oxide "continuum" were all made under sufficiently low resolution (seldom better than 5-10Å) that they are "continuum" more by definition than by observation.

Pertinent Laboratory Results

Figure 1 shows a broad chemiluminescent emission from the diatomic molecule BaO* produced in the reaction

$$Ba + N_2O \rightarrow BaO^* + N_2 \quad , \tag{14}$$

under molecular beam conditions by Zare and co-workers.[29] The reaction of Ba with O_3.

$$Ba + O_3 \rightarrow BaO + O_2 \quad , \tag{15}$$

produces a nearly identical spectrum.[30] Similar broad emissions due to excited alkali halide molecules have been observed in the reaction of alkali metal dimers with halogen molecules.[31]

Figure 2 shows a spectrum obtained with Zare's apparatus for the reaction of Al with O_3.[0] The identification of the AlO (B → X) emission protruding above the chemiluminescent "continuum" in the 4500-5000Å range shows that one pathway for this reaction is

$$Al + O_3 \rightarrow AlO^* + O_2 \cdot \quad 7 \tag{16}$$

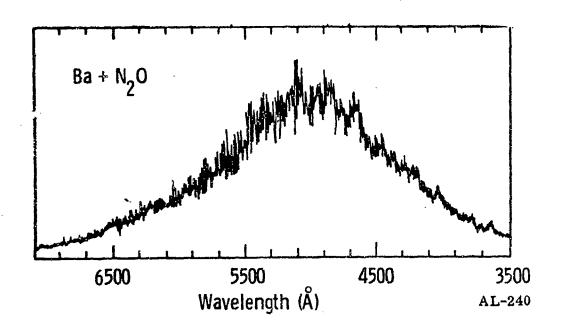Figure 1 – BaO[*] Emission From the Reaction of Crossed Molecular Beams of Ba and N$_2$O (Note: The reaction Ba + O$_3$ produces a nearly identical spectrum (See Ref. (30))).
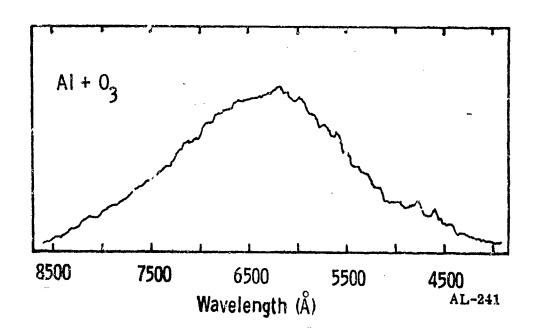

Figure 2 – Chemiluminescent Emission From the Reaction of Crossed Molecular Beams of Al and O$_3$ (Note: Emission of the dipole allowed AlO (B → X) transition is superimposed on the broad continuum-like emission (See Ref. (6))).

8

The creation of AlO_2^* is thermodynamically possible under the single collision conditions in crossed molecular beams,

$$Al + O_3 \rightarrow AlO_2^* + O \qquad . \qquad (17)$$

However, the formation of AlO_2, which has the symmetric structure O-Al-O,[32] requires insertion of the aluminum atom into one of the $O-O_2$ bonds in O_3. This type of insertion reaction can be expected to have a much higher activation energy than the simple atom abstraction of reaction (16). In addition, the simple atom abstraction mechanism is found to predominate for nearly all of the atom-small molecule reactions studied by molecular beam techniques to date.[33] Thus, it is tempting to ascribe all of the chemiluminescent emission shown in Fig. 2 to AlO*.

Very recently, Broida and co-workers studied the BaO* emission from the reaction of Ba with N_2O. They found that the emission can change (at pressures of a few torr or higher) from the broad emission of Fig. 1 to a well-resolved spectrum characteristic of the BaO $(A\,^1\Sigma^+ \rightarrow X\,^1\Sigma^+)$ transition.[34] These observations are explained by postulating the creation of BaO* by reaction (14) in the long-lived $(a\,^3\Pi)$ excited state. This is followed by collisional transfer into the $(A\,^1\Sigma^+)$ state which has a shorter radiative lifetime.[35] Quantitative measurements show that the BaO* pumping process occurs with an efficiency of greater than 20%.[34, 35]

Data for the $Ba + N_2O$ reaction have been presented to indicate that a diatomic molecule such as BaO can produce a broad chemiluminescent emission when metastable, excited electronic states are efficiently pumped by chemical reaction. Aluminum monoxide also has a number of such bound long-lived electronic states which are thermodynamically accessible to chemical pumping reactions such as reaction (16). Several additional exothermic reactions pertinent to conditions characteristic of both laboratory and upper atmospheric glows will be proposed later.

Figure 3 shows potential energy curves calculated by H. Michels[36] for the lowest bound states of AlO. Candidate states for the upper levels which might produce the "continuum" radiation include the lowest lying $^4\Sigma^+$ and $^4\Pi$ states, as shown in Fig. 3, and the high vibrational levels of the $(A\,^2\Pi)$ state, which has been experimentally characterized by McDonald and Innes.[37]

9

Subsequent sections of this report will deal with exothermic reactions capable of producing AlO in these excited states. In particular, reactions of aluminized grenade products with atomic oxygen (along with reaction (16)) will be examined in depth to identify pathways which efficiently populate the (A $^2\Pi$), $^4\Pi$, and $^4\Sigma^+$ states at the expense of the X and B states. Brief discussions of Ba and alkali dimer reactions will be presented where parallel mechanisms are expected. A discussion of trimethyaluminum oxidation by atomic oxygen is also presented, along with candidate AlO* pumping reactions for TMA flames and atmospheric releases.
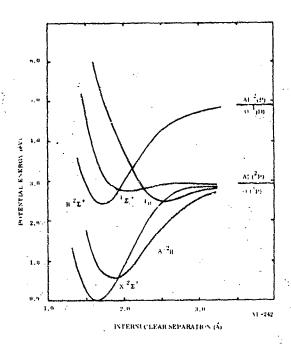
Figure 3 – Calculated Lowest Bound States of AlO.[36]

Grenade Pumping Reactions

The aluminized grenades which produced the chemiluminescent glows described in Refs. (11), (12), (13), (16), and (17) contained a little over five moles of aluminum powder mixed with approximately 1.3 moles of an oxidizer such as KNO_3 or a mixture of $BaNO_3$ and $KClO_4$. They also contained a 20g tetryl exploder, and a booster consisting of 0.2 mole TNT and 1.2 additional moles of powdered aluminum.

10

Little information is given on the expected explosion products of these grenades, but they are oxidizer-poor, and can be expected to produce appreciable unoxidized aluminum. This expectation is borne out by the observation in twilight releases of solar-pumped aluminum doublets at 3944-3961 and 3082-3093Å.[12]

A closely related, but better characterized, release system is the steel burner used by Rosenberg, et al., to release the reaction products of an explosive $CsNO_3$-Al powder mixture.[10] Thermochemical calculations of the pressure, temperature, and products of this reacting mixture when the reaction is at equilibrium are also presented in Ref. (10). This reaction mixture was calculated to contain 35, 7, and 2.5 mole-percent of Cs, Al, and AlO vapor, respectively, before the reaction products were vented through a converging nozzle with a half-centimeter orifice.[10]

In order to invoke AlO* as the source of the chemiluminescent emission observed for releases utilizing the inorganic grenades and burner described above, it is necessary to show that such devices produce molecular species containing a weakly bound aluminum atom which can react with atmospheric, atomic oxygen to produce AlO*. A reasonable candidate species is the aluminum dimer, Al_2. This species has been observed spectroscopically by Innes and co-workers,[38] and mass spectrometrically by Chupka and co-workers, who determined a bond energy of 2.0 eV.[39] A bond energy of 1.7 eV has also been proposed.[40] Since the bond energy of AlO is close to 5.2 eV,[6,37] the reaction between Al_2 and atomic oxygen,

$$Al_2 + O \rightarrow AlO^* + O \quad ,\tag{18}$$

is exothermic by more than 3.2 eV, or 74 kcal/mole, if ground-state products are formed. This compares to the $Al + O_3$ exothermicity of 4.1 eV.[6] Reactions (16) and (18) are thus thermodynamically able to produce AlO* in the (A $^2\Pi$), (B $^2\Sigma^+$), $^4\Pi$, and $^4\Sigma^+$ states according to Michels' calculations.

Aluminum dimers can be expected to form as the grenade or burner reaction products expand and cool. Indeed, the formation of Na and NO dimers has been previously invoked to explain the chemiluminescent emissions observed in the upper atmospheric release of these substances.[41,42]

11

The unknown details of grenade fragmentation make the fluid-dynamic modeling of the grenade release difficult, and prevent the calculation of the extent of Al dimerization. However, Al_2 formation in the burner nozzle expansion utilized by Rosenberg, et al., can be treated by using the parameterized theory developed by Gordon, Lee, and Herschbach.[43] By using an Al_2 dissociation energy of 2.0 eV,[39] the Al_2 spectroscopic parameters of Innes,[38] and a long-range van der Waals attraction constant equal to that for Na, the Al_2 dimerization parameters, as defined by Gordon, et al., are $T_d = 23210\ ^OK$, $\rho_d = 1.62\ g/cm^3$, and $\omega_d = 2572\ cm$. The equilibrium burner conditions published by Rosenberg, et al., give the temperature, density, and nozzle orifice release parameters as $T = 4100\ ^OK$, $\rho = 4 \times 10^{-3}\ g/cm^3$, and $\omega = 0.5\ cm$. The division of the Al_2 parameters into the release parameters produces the reduced variables $\bar{T} = 0.177$, $\bar{\rho} = 2.5 \times 10^{-3}$, and $\bar{\omega} = 1.94 \times 10^{-4}$. Projection of these reduced parameters onto the parametric dimerization curves published by Gordon, et al., indicates that greater than 80% of the Al released by the AFCRL burner[10] will be dimerized. Of course, the burner release products are a complex chemical mixture, and chemical reactions other than Al dimerization may take place during the expansion. For instance, an unknown portion of the Al atoms may combine with the more abundant atomic Cs to form CsAl. However, CsAl can be expected to have a bond strength on the order of one electron-volt, and would serve as an equally good precursor for AlO*:

$$CsAl + O \rightarrow AlO* + Cs \qquad . \qquad\qquad (19)$$

Similarly, the potassium-loaded grenades may form KAl, which could also serve as an AlO* precursor:

$$KAl + O \rightarrow AlO* + K \qquad . \qquad\qquad (20)$$

Several theoretical aspects of the $Al_2 + O$ reaction as the prototype grenade pumping reaction are discussed in detail below. The $Al + O_3$ reaction of Zare's experiment[6] is also considered in this theoretical treatment.

12

According to the mechanisms proposed above, both the grenade reaction and the ozone reaction produce chemiluminescence from AlO due to the population of the lowest-lying $^2\Pi$, $^4\Sigma^+$, and $^4\Pi$ states. The unresolved, apparently continuous emission attributed to these states, which we refer to collectively as the Y states, is much more intense than the emission from the (B $^2\Sigma^+$) states. The correlation of the electronic states of the reactants and products in the Al_2+O and $Al+O_3$ reactions is examined below for factors which may favor population of the Y states rather than the B state. One such factor is evident, and since it is a property of the AlO molecule itself, it can be expected to operate in all reaction processes which produce AlO. This is the fact that the Y states correlate with ground-state Al + O atoms, whereas the B state correlates with a ground Al atom + excited O atom (see Fig. 3). Consequently, it is plausible that the potential energy surfaces leading to the Y states provide more favorable pathways than the potential energy surface leading to the B state.

The reaction $Al_2 + O \rightarrow AlO + Al$

For the reactants, two channels are considered, corresponding to interaction without and with electron transfer:

(a) $Al_2 \left(^3\Sigma_g^-\right) + O \left(^3P_g\right)$

(b) $Al_2^+ \left(^2\Pi_u\right) + O^- \left(^2P_u\right)$.

The identification of the Al_2 ground state as $^3\Sigma_g^-$ is based on spectroscopic evidence and the expected molecular orbital configuration,[38] and the assignment of Al_2^+ as $^2\Pi_u$ is a corollary.

For the products, four channels are considered:

(a') $AlO \left(^2\Sigma^+\right) + Al \left(^2P_u\right)$

(b') $AlO \left(^2\Pi\right) + Al \left(^2P_u\right)$

13

$$\text{(c')} \quad \text{AlO} \left({}^{4}\Sigma^{+} \right) \; + \; \text{Al} \left({}^{2}P_{u} \right)$$

$$\text{(d')} \quad \text{AlO} \left({}^{4}\Pi \right) \; + \; \text{Al} \left({}^{2}P_{u} \right) \quad .$$

Channel (a') corresponds to production of AlO in either the ground X state or the B state; channels (b'), (c'), and (d') constitute the Y states. Table I gives the spin correlations for these channels and Table II the spatial-state correlations pertaining to collinear Al-Al-O configurations. The determination of state correlations is fully described by Herzberg.[44] Channel (a) gives rise to singlet, triplet, and quintet potential surfaces which correlate, respectively, with (a', b'), (a', b', c', d'), and (c', d'), whereas (b) gives singlet and triplet surfaces which correlate, respectively, with (a', b'), and (a', b', c', d'). Thus, as far as spin correlations are concerned, all the product channels can be populated, whether or not the reaction involves an electron transfer. In assessing the spatial correlations, the reaction is not postulated to be constrained to collinear configurations. However, the fact that all the reactant and product channels correlate (via Σ^{+} + Π surfaces) for collinear configurations serves to demonstrate that they will also correlate for noncollinear configurations. This holds because the transition from reactants to products

TABLE I. SPIN CORRELATIONS FOR Al$_2$ + O REACTION

	Reactants		Intermediate	Products	
(a)	Triplet +	Triplet	Quintet	Quartet +	Doublet (c', d')
	$s = 1$	$s = 1$	$s = 2$	$s = \frac{3}{2}$	$s = \frac{1}{2}$
			Triplet		
			$s = 1$		
(b)	Doublet +	Doublet	Singlet	Doublet +	Doublet (a', b')
	$s = \frac{1}{2}$	$s = \frac{1}{2}$	$s = 0$	$s = \frac{1}{2}$	$s = \frac{1}{2}$

14

TABLE II

TABLE II. SPATIAL-STATE CORRELATIONS FOR COLLINEAR $Al_2 + O$ REACTION

Reactants	Intermediate	Products

(b) $\Pi_u + P_u$	Δ Π Σ^-	$\Pi + P_u$ (b', d')
(a) $\Sigma_g^- + P_g$	Σ^+	$\Sigma^+ + P_u$ (a', c')

preserves no molecular symmetry elements except in the collinear case. Hence, restrictions on the correlation of reactant and product states can only occur for the collinear case. When such restrictions exist, they are significant for other configurations, as well, because states that do not interact in the collinear case will couple only weakly for a substantial range of noncollinear configurations.

The reaction $Al + O_3 \rightarrow AlO + O_2$

Again, reactant channels with and without electron transfer are considered:

(a) $Al\left(^2P_u\right) + O_3\left(^1A_1\right)$

(b) $Al^+\left(^1S_g\right) + O_3^-\left(^2B_1\right)$.

Two sets of four channels are considered for the products. As before, these are labelled (a', b', c', d') to distinguish the electronic states of AlO; a single prime indicates that the accompanying O_2 molecule is in its ground $^3\Sigma_g^-$ state, while a double prime indicates O_2 is in the lowest-lying excited $^1\Delta_g$ state. Table III gives the spin correlations. In this case, the reaction proceeds on a doublet potential surface whether or not electron transfer occurs. All the product channels except (c'', d'') can be populated from this doublet surface. Table IV gives the spatial-state correlations for "isoceles" configurations. In these configurations, which are the only ones that preserve a symmetry element in the reaction, the Al atom approaches along the two-fold axis of O_3, whereas the products emerge with the Al-O bond along this axis and the O-O bond perpendicular to it. In such configurations, the reaction without electron transfer can go via A_1, B_1, and B_2 potential surfaces, and thus populate any of the product channels. The reaction with electron transfer goes only via a B_1 potential surface, but can populate all the product channels except (b', d'). We again conclude that there are no significant state correlations which favor producing AlO in the Y states rather than in the B state.

TABLE III. SPIN CORRELATIONS FOR Al + O_3 REACTION

Reactants	Intermediate	Products

16
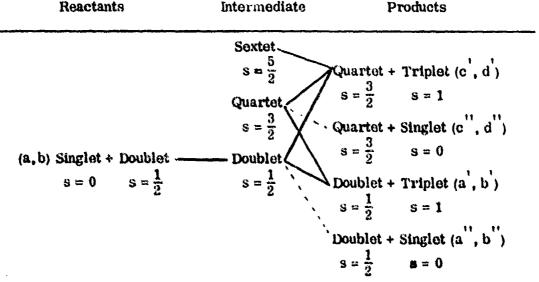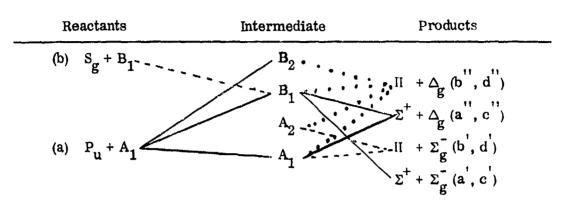
TABLE IV. SPATIAL-STATE CORRELATIONS FOR ISOCELES Al + O_2 REACTION

Reactants	Intermediate	Products

(b) $S_g + B_1$

(a) $P_u + A_1$

B_2

B_1

A_2

A_1

$\Pi + \Delta_g (b'', d'')$

$\Sigma^+ + \Delta_g (a'', c'')$

$\Pi + \Sigma_g^- (b', d')$

$\Sigma^+ + \Sigma_g^- (a', c')$

Qualitative Electronic Aspects

The analysis of correlations given above has dealt only with the question of whether interactions linking reactant and product states are or are not allowed by the spin and spatial symmetry properties of the electronic states. Of more practical interest is the question whether an allowed interaction is strong or weak, since this determines the favored reaction pathway. Here the likely pathways are discussed in terms of qualitative chemical bonding concepts. Very similar interpretations have proved useful in other studies of the reactions of metals with electrophilic reagents[45] as we shall illustrate later for some analogous chemiluminescence processes.

Electron transfer from the metal to the electrophilic molecule is the basic feature, as indicated in Fig. 4. The electron transfer can occur when the energy Δ required to form the ion-pair $A^+ + (BC)^-$ is offset by the coulombic attraction. Thus, the coulombic potential curve (dotted) crosses the asymptote for the A + BC interaction (dashed) at a distance r_c given by $e^2/r_c = \Delta$. The ionization potential
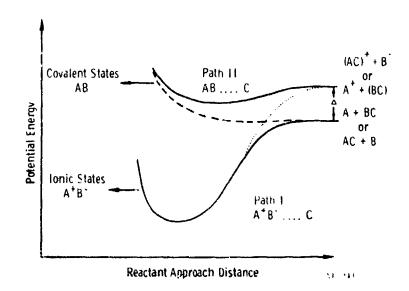
Figure 4 – Schematic Potential Energy Surfaces for Reactant Channel Interaction of a Metal A and an Electrophilic Molecule BC or a Metal Dimer AC + Electrophilic Atom B. (Note: The Quantity Δ Denotes the Energy Required to Form the Ion-Pair $A^+ + (BC)^-$ or $(AC)^+ + B^-$ at Infinite Separation; Δ is Given by the Difference in Ionization Potential of A (or AC) and the Electron Affinity of BC (or B).)

is ~6 eV for both Al and Al_2. The electron affinity is ~1.5 eV for O, and ~2.5 eV for O_3. Therefore, the crossing radius is about $3.2\overset{\circ}{A}$ for $Al_2 + O$, and about $4.1\overset{\circ}{A}$ for $Al + O_3$. These values of r_c are much larger than the AlO bond distance (~$1.7\overset{\circ}{A}$), but small enough to ensure strong interaction of the $A^+ + (BC)^-$ and A + BC states (unless precluded by symmetry). The adiabatic potential surfaces (solid curves) resulting from this interaction are thus well separated in the crossing region. Therefore, we expect that the dominant reaction path will be the lower energy surface (labeled Path I), since the collision energy is too low to allow direct access to the higher energy surface (labeled Path II). If no complicating factors intervene, the lower surface will lead to formation of ground-state product molecules. This simple picture predicts no chemiluminescence beyond a very feeble contribution from non-adiabatic transitions to the upper states.

15

There are two important complicating factors:

1) The nature of the AlO states resulting from open-shell electronic structure. It will be shown that Path I in Fig. 4 is expected to lead primarily to the formation of the (A $^2\Sigma$) excited state of AlO rather than the ground (X $^2\Sigma$) state.

2) The multiplicity of reactant states resulting from Al and O being open-shell P atoms. This provides adiabatic routes to Path II in Fig. 4, and thus allows population of the $^4\Pi$ and $^4\Sigma$ excited states of AlO.

Since the chemical bonding in metal oxides is largely ionic, the simple ion-pair model is a useful starting point in the qualitative analysis of the AlO states. If Al^+ approaches O^-, the hole in the oxygen valence shell has two possible locations: the $2p\sigma$ oxygen orbital along the internuclear axis or the $2p\pi$ oxygen orbital transverse to the axis. The corresponding molecular orbital configurations are $\sigma\pi^4$ and $\sigma^2\pi^3$, respectively, and the corresponding electronic states of Al^+O^- are $^2\Sigma$ and $^2\Pi$, respectively. According to the simple ionic model, the $^2\Pi$ state should be below $^2\Sigma$ because the oxygen p orbital directed towards Al^+ contains two electrons in the $^2\Pi$ state, but only one in the $^2\Sigma$ case. As shown in Fig. 3, the spectroscopic data and electronic structure calculations indeed find the (A $^2\Pi$) state to be more stable than the (X $^2\Sigma$) state down to distances of $\sim 1.8\overset{o}{A}$, although (X $^2\Sigma$) lies lower at the equilibrium internuclear distance. A recent analysis of metal-oxygen bonding suggests that covalent bonding with the pair of s electrons of Al^+ makes $^2\Sigma$ more stable than $^2\Pi$ at short distances.[46] In the chemical reaction, however, the situation at larger distances is more significant.

Any reaction which forms AlO via an electron-jump process akin to Path I of Fig. 4 can thus be expected to produce predominantly the (A $^2\Pi$) state, simply because this puts two electrons in the p orbital directed towards the Al^+ ion, whereas the (X $^2\Sigma$) state has only one electron in that orbital. It should be noted that any AlO (A) formed via either $Al + O_3$ or $Al_2 + O$ can be expected to be highly vibrationally excited. In fact, Gole and Zare have observed AlO* (B) up to $v = 18$ in the $Al + O_3$ reaction.

19

Excitation of the $^4\Pi$ or $^4\Sigma$ states of AlO corresponds to Path II of Fig. 4. The molecular orbital configuration of those states is indicated in Fig. 5, which shows that they can be considered to arise from the transfer of one of the 3s electrons of the Al atom to the O atom, just as the $^2\Pi$ and $^2\Sigma$ states arise from transfer of the 3p electron. Actually, the bonding in these quartet states has much more covalent character than in the corresponding doublet states since the higher ionization potential for the 3s orbital prohibits electron transfer until a much closer approach. This also implies that, aside from multiplicity factors, the cross sections for forming the quartet states will be substantially smaller than for the doublet states.

In some cases, however, spin multiplicity may have a major role. In the $Al_2 + O$ reaction, the spin correlations of Table I show that the quintet potential surfaces lead adiabatically to formation of AlO in the $^4\Pi$ and $^4\Sigma$ states. This path might be inhibited by a potential barrier, and electronic structure calculations or experiments would be required to determine whether such a barrier exists. A somewhat analogous example which has no barrier is the recombination of nitrogen atoms (these are ^{4}S atoms); the celebrated "active-nitrogen" afterglow has been shown to come from a bound-quintet excited state of the nitrogen molecule.[47] If

Figure 5 - Molecular Orbital Configurations for AlO States.

20

there is no barrier inhibiting the quintet component of the $Al_2 + O$ reaction, the statistical weight factor (2s + 1 degeneracy) will form it over the triplet and singlet routes in the ratio $5/(3 + 1) = 5/4$. Since the singlet and triplet surfaces also correlate with the $^4\Pi$ and $^4\Sigma^+$ states, an even larger fraction than 5/4 of the adiabatic reactions of $Al_2 + O$ may populate these states.

Spin multiplicity has no direct role in the $Al + O_3$ reaction, which goes via a doublet surface, as shown in Table II. In this case, the spatial degeneracy of the reactant states still fosters excitation of the $^4\Pi$ and $^4\Sigma$ states of AlO, however, as seen in Table IV. Each of the three available potential surfaces (A_1, B_1, B_2) can form either the $^4\Pi$, $^4\Sigma$ states or the $^2\Pi$, $^2\Sigma$ states of AlO. Only one (B_1) correlates with electron transfer via the $Al^+ (\ldots 3 s^2) + O_3^-$ ion-pair. Thus the other two surfaces (A_1 and B_2) are likely to involve largely covalent interaction, and thereby form the $^4\Pi$, $^4\Sigma$ states of AlO more readily than the $^2\Pi$, $^2\Sigma$ states.

The excited (B $^2\Sigma^+$) state of AlO lies far above the (X $^2\Sigma^+$) and (A $^2\Pi$) states, and, at large internuclear distances, also lies far above the $^4\Pi$ and $^4\Sigma$ states (see Fig. 3). Thus, the B state is much less likely to be produced in the reaction, as already noted. Of course, it might be excited in a subsequent collision process.

Analogous Reaction Mechanisms

Other chemiluminescent reactions of metals with electrophilic molecules are briefly outlined below to bring out points of resemblance to the aluminum reactions discussed above.

Reaction of alkali dimers with halogens

Recent experiments have shown that a very broad molecular emission results from the reaction

$$K_2 + Cl_2 \rightarrow KCl^* + KCl \quad ,$$

and numerous related reactions.[31] Under low resolution ($\sim 15\text{-}20\overset{o}{A}$), the emission appears continuous, but higher resolution ($< 5\overset{o}{A}$) reveals a long progression of vibrational bands.[48] The spectrum has now been shown to come from an excited

21

state of KCl which has some similarity to the $^4\Pi$, $^4\Sigma$ states of AlO. The ground state for KCl again has ionic bonding, $K^+ Cl^-$. Since this is a closed-shell structure, the simple picture of Path I in Fig. 4 applies, and the ground state is nondegenerate (rather than split into the X and A components, as in AlO). The lowest excited states, which correspond to Path II, consist of a $^1\Sigma^+$, $^3\Sigma^+$, $^1\Pi$, $^3\Pi$ set, which correlates with unexcited $K\left(^2S_{1/2}\right)$ and unexcited Cl atoms (including both the $^2P_{3/2}$ and $^2P_{1/2}$ spin-orbit components). These latter states involve covalent bonding. One or two have shallow wells, which give the observed chemiluminescence, while the others are repulsive, in close analogy to the AlO states. Likewise, there is a higher excited KCl state analogous to the B state of AlO, but chemiluminescence from this state is not seen, although the reaction exoergicity is sufficient to produce it. Our interpretation of the aluminum case thus is consistent with this somewhat simpler system.

Reaction of Ba with N_2O and O_3

Chemiluminescence observed when a Ba atom beam traverses a scattering chamber filled with N_2O at low pressure ($\sim 5 \times 10^{-4}$ torr) has a complex, many-line, headless spectrum.[29] An identical spectrum is found for the Ba + O_3 reaction.[30] The broad emission has been attributed to the (a $^3\Pi$) state of BaO,[35] which again bears some analogy to the $^4\Pi$, $^4\Sigma$ state of AlO.

As noted previously, the complex, many-line spectrum gives way to well-defined bands of the BaO* (A $^1\Sigma^+ \rightarrow$ X $^1\Sigma^+$) progression at pressures of a few torr or more of Ar buffer.[34] This observation indicates that the Ba + N_2O reaction populates the (a $^3\Pi$) state with a quantum efficiency of 0.2 or greater, and that the (a $^3\Pi$) state is then collisionally perturbed into the A state.[34,35] It seems reasonable to attribute the appearance of the AlO (B $\rightarrow$X) emission observed as the pressure is raised in the reaction of TMA and atomic oxygen[3] to a similar collisionally induced electronic transition from one of the Y states to the B state.

22

As noted above, trimethlylaluminum (TMA) forms a stable vapor-phase dimer with a dissociation energy of 20.2 kcal/mole. The prevailing method of releasing TMA in upper atmospheric release experiments is to eject the room temperature liquid at high pressures through small orifices into the atmosphere, where a portion of it flash vaporizes, and the rest freezes.[14] Under these conditions, most of the vapor-phase TMA will, at least initially, be in the dimeric form.

The TMA dimer exists in a diborane-like structure, with two methyl groups sigma-bonded to each aluminum, and with the two additional methyl groups in a bridging configuration between the aluminum atoms, forming three-center Al-C-Al bonds.[49] No successful kinetic mechanism for the oxidation of TMA by atomic oxygen appears to have been published despite flow-tube studies of the TMA - atomic oxygen reaction,[1-3, 5] and studies of premixed TMA/O_2 flames.[4] Studies of the interaction of TMA with O_2 indicate that the first step of the reaction is the insertion of molecular oxygen into one of the Al-CH_3 bonds[50] (the weakest bonds in the molecule). This is consistent with the general concept that an electrophilic reagent will attack the negatively charged carbon atom in an alkyl-metal bond.[49] This insertion is also consistent with the studies of Cullis, et al., which demonstrated that the combustion of TMA and O_2 proceeds via a free radical mechanism.[51]

It seems reasonable to presume that the very fast attack of atomic oxygen on either monomeric or dimeric TMA proceeds by a similar insertion step:

$$(21)$$

or

$$(22)$$

where $\ddagger$ denotes vibrational excitation. It also seems reasonable to presume that the unstable product of reactions (21) or (22) will decay by the exothermic pathway:

23

$$\text{(CH}_3\text{)}_2\text{Al}(\mu\text{-CH}_3)_2\text{Al(CH}_3\text{)(OCH}_3\text{)} \longrightarrow (\text{CH}_3)_2\text{Al}(\mu\text{-CH}_3)_2\text{Al}-\text{CH}_3 + \text{H}_2\text{CO} + \text{H} \qquad (23)$$

or

$$\text{(CH}_3\text{)}_2\text{Al(OCH}_3\text{)} \longrightarrow (\text{CH}_3)_2\text{Al} + \text{H}_2\text{CO} + \text{H}\ . \qquad (24)$$

The heat of reaction for the overall reactions, $[(21) + (23)]$ and $[(22) + (24)]$, can be calculated from the average Al–CH_3 bond strength in TMA (62.9 – 64.5 kcal/mole),[26], [27] the standard heats of formation of H, OCH_2, and CH_3,[52] and, in the case of the reaction $[(21) + (23)]$, the TMA dimerization energy.[26] The results of these calculations indicate that reaction $[(21) + (23)]$ is 3 to 6 kcal/mole exothermic, while the reaction $[(22) + (24)]$ is 6 to 9 kcal/mole exothermic. However, if the product of the reactions is H_3CO rather than $H_2CO + H$, the exothermicity will be much greater, and the products could contain a large amount of internal energy. A similar attack on the products of reactions (23) and (24),

$$(\text{CH}_3)_2\text{Al}(\mu\text{-CH}_3)_2\text{Al}-\text{CH}_3 + \text{O} \longrightarrow \text{Al}_2(\text{CH}_3)_4 + \text{OCH}_2 + \text{H} \qquad (25)$$

or

$$\text{CH}_3 - \text{Al} - \text{CH}_3 + \text{O} \longrightarrow \text{CH}_3 - \text{Al} + \text{OCH}_2 + \text{H}\ , \qquad (26)$$

will produce either $AlCH_3$ directly (reaction (26)), or $Al_2(CH_3)_4$ (reaction (25)), which may or may not spontaneously decay to TMA and Al–CH_3:

24

$$Al_2(CH_3)_4 \rightarrow Al\,CH_3 + Al\,(CH_3)_3 \quad . \tag{27}$$

In any event, if at this point an attacking oxygen atom reacts with the now unshielded Al atom in either $AlCH_3$ or $Al_2(CH_3)_4$, a very exothermic path for the production of AlO* is possible:

$$Al-CH_3 + O \rightarrow AlO* + CH_3 \tag{28}$$

$$Al_2(CH_3)_4 + O \rightarrow AlO* + Al\,(CH_3)_3 + CH_3 \quad . \tag{29}$$

The exothermicity of reaction (28) (or reaction (29) if reaction (26) does not occur) can be expected to be greater than 55 kcal/mole for the production of ground-state products. Thus, reactions (28) and (29) could produce AlO* in the (A $^2\Pi$) state at very high vibrational levels, and may be sufficiently exothermic to populate the $^4\Pi$ and/or $^4\Sigma^+$ states.

25

AlO* MECHANISM APPLIED TO RELEASE DATA

In this section the AlO* production reactions proposed above ((18)-(20) for grenade-like releases and (28)-(29) for TMA releases) will be examined to see if they are compatible with quantitative observations from upper atmospheric experiments. Upper atmospheric glow characteristics which must be at least qualitatively explained by any candidate mechanism for the chemiluminescent emission include the duration of the glow, the total radiant output, and the dependence of these two functions on altitude.

At altitudes below 100 km, grenade-produced chemiluminescence decreases monotonically after release, while at higher altitudes, the initial bright flash is followed by a one- to two-second build-up in radiant intensity (100-125 km), or by a brief fall-off in radiant intensity (>125 km), which then builds back to a secondary maximum within 10 sec after detonation.[13] The effective time duration of the grenade glows is one to two minutes. At 105 km, the total radiant power emitted has fallen by a factor of 10 at the end of one minute, while at 140 km, it has fallen by a factor of four.[13,17] The total number of photons emitted by the nighttime grenade glows increases by two orders of magnitude between 105 and 120 km, while above 120 km it appears to plateau.[13]

A simple physical model of atmospheric releases can be based on the rapid expansion of the released gases until pressure equilibration is reached. In the case of aluminized grenades, Linevsky and Alyea have calculated that this equilibration is reached within four seconds for the altitudes of interest.[3] After a pressure balance is reached, the further mixing of atmospheric and release gases is controlled by diffusive processes. This model is slightly complicated by the fact that in a high-temperature release, the release gases may be hotter than the ambient atmosphere, even after pressure equilibration has occurred.[3]

The volume of the initial expansion cloud can be approximated by

$$\frac{4}{3} \pi R_0^3 = \frac{N}{n} \quad , \tag{30}$$

26

where R_0 is the radius of the cloud at the pressure balance point, N is the total number of molecules released, and n is the cloud molecular number density, which can be defined, in terms of the ambient number density n_∞, the cloud temperature T, and the ambient atmospheric temperature T_∞, by

$$n = n_\infty \left(\frac{T_\infty}{T}\right) . \tag{31}$$

A reasonable estimate for the total molecular output of either the Australian grenades or AFCRL burner is 10 moles, or 6×10^{24} molecules. Assuming a cloud temperature equal to twice the ambient temperature and using the ambient number densities of Jacchia[23] yields the R_0's listed in Table V:

$$R_0 \approx \left(\frac{3}{2\pi} \frac{N}{n_\infty}\right) cm \approx \left(\frac{3}{2\pi} \frac{6 \times 10^{24}}{n_\infty}\right)^{1/3} cm \tag{32}$$

TABLE V. GRENADE AND BURNER CLOUD RADII AT PRESSURE EQUILIBRATION

Altitude (km)	n_∞ (molecules/cm^3)	R_0 (cm)
100	1.20×10^{13}	6.2×10^3
110	2.26×10^{12}	10.8×10^3
120	5.78×10^{11}	17.0×10^3
140	9.79×10^{10}	30.8×10^3

These calculated R_0's can be used to make two points. First, all of the initial grenade products cannot be completely oxidized during this initial pressure equilibration period. By using Jacchia's atomic oxygen densities and the volume implied by the calculated R_0's, it can be seen that the initial expansion volume contained only 2.0×10^{24} oxygen atoms at 100 km, and 1.1×10^{24} O atoms at 140 km. This is less than one O atom per molecule of released product, and shows that the complete oxidation of the released products will have to proceed on a time scale of diffusive rather than explosive mixing.

27

Secondly, the increasing total photon yield with increasing altitude between 95 and 120 km can be qualitatively understood by realizing that the smaller expansion clouds allow reactions between the initial release products, thereby removing the weakly bound aluminum atoms needed to produce AlO* via the prototype reactions (18)-(20). An example of such a reaction would be

$$Al_2 + AlO \longrightarrow Al_2O + Al \qquad (33)$$

Each such reaction would reduce the amount of light emitted unless the product was electronically excited. By assuming that these product-product reactions have a rate constant of $k_{31} = 1 \times 10^{-12}$ cm^3/sec, and that 10% of the release products can react with the loosely bound Al, the characteristic reaction time in the pressure-balanced cloud would be

$$\tau_{chem} \approx \frac{1}{k_{31}\left(0.1N/\frac{4}{3}\pi R_0^3\right)} = \frac{4.19\ R_0^3}{(1 \times 10^{-12})\ (6 \times 10^{23})}\ \text{sec} \qquad (34)$$

For an altitude of 100 km, $\tau_{chem} = 1.7$ sec, while for an altitude of 120 km, $\tau_{chem} = 34$ sec. Thus, at lower altitudes, considerably less of the weakly bound aluminum survives the initial mixing phase to interact with ambient atomic oxygen. This picture of product-product interactions is consistent with the fact that at altitudes below 90 km, neither grenade-like nor TMA releases produce chemiluminescent emissions beyond an initial, short-lived flash. A secondary cause of the grenade-glow altitude dependence may be the loss of loosely bound Al to reactions with molecular oxygen which do not lead to electronically excited products.

It should also be noted that the TMA oxidation scheme proposed in the preceding section would not appear to be particularly sensitive to reactions between release products, and that, therefore, total TMA chemiluminescent output should not show the sensitive altitude dependence displayed by grenade releases between 95 and 120 km. Indeed, total TMA chemiluminescence should only be weakly altitude-dependent at altitudes above 100 km, where sufficient atomic oxygen mole fractions exist to support reactions (28)-(29). Below 90-100 km, the destruction of species such as Al-CH$_3$ by molecular oxygen can be expected to greatly reduce chemiluminescent output.

28

The total cloud glow time of one to two minutes for the grenade-produced glows can be explained by noting that, after the initial expansion to pressure balance, the diffusive mixing of the release products with the atmosphere is always slower than the reaction times for reactions (18)-(20). Reactions (18)-(20) can be expected to proceed with a rate constant on the order of 10^{-10} cm^3/sec. By using Jacchia O-atom number densities of 3.72×10^{11} cm^{-3} at 110 km and 3.77×10^{-10} cm^{-3} at 140 km, characteristic reaction times τ_{AlO*} are estimated to be 27 msec at 110 km, and 265 msec at 140 km.

$$\tau_{AlO*} = \frac{1}{k_{(18)-(20)} \times [O]} \quad \text{sec} \tag{35}$$

However, the characteristic diffusion time for the atmosphere to penetrate the pressure-balanced release cloud (and the release cloud to expand into the atmosphere) can be estimated by

$$R_0 = \sqrt{D \tau_{diff}} \tag{36}$$

or

$$\tau_{diff} = \frac{R_0^2}{D} ,$$

where D is the neutral diffusion coefficient in units of cm^2/sec. Measurements of D from grenade and TMA release clouds have been presented by Golomb and MacLeod,[15] who recommend a value of 6×10^7 for 140 km and 2×10^6 for 110 km. Thus, the characteristic diffusion time for cloud-atmosphere mixing, and, therefore, the characteristic time for AlO* pumping reactions, is 58 sec at 110 km, and 16 sec at 140 km. The total glow from grenade-like release clouds can be expected to last a few times τ_{diff}, or one to two minutes.

An identical analysis holds for TMA release clouds, with the exception that TMA oxidation products such as OCH_2, OCH, etc., will compete very effectively with reactions (28)-(29) for atomic oxygen, and at least three oxygen atoms are needed to produce AlO* from TMA in the first place. Thus, significantly more

29

atomic oxygen will be needed to produce the same amount of light in equal molar grenade-like and TMA releases. This increase in atomic oxygen consumption per photon emitted will require that TMA glows have characteristic diffusion times two to four times longer than similar size, grenade-like releases. It is therefore not surprising that TMA glows can sometimes be observed up to five minutes after release.[53]

Finally, detailed analysis of the prototype AlO* pumping reaction between Al_2 and O indicates that the population of the emitting Y states by such reactions can be efficient enough to support the apparently large chemiluminescence quantum yields observed in upper atmospheric experiments.

RECOMMENDED LABORATORY EXPERIMENTS

A number of laboratory experiments are possible to test the hypothesis that the aluminum-oxygen chemiluminescence continuum is due to emission from some combination of the (A $^2\Pi$) and lowest-lying $^4\Sigma^+$ and $^4\Pi$ states of AlO.

One of the most direct ways of identifying AlO* in the (A $^2\Pi$) state is to induce fluorescence in the AlO emission bands by laser pumping. McDonald and Innes have demonstrated that emission bands near $2800\overset{o}{A}$ arise from transitions between the $^2\Sigma^+$ state at 40,300 cm^{-1} and the A state, while emission near $2500\overset{o}{A}$ occurs between a $^2\Delta_i$ state and the A state.[37] In addition, it may be possible to pump lower levels of the A state to the (B $^2\Sigma^+$) state, and observe the green B $\rightarrow$ X emissions.

A second method of confirmation would involve the simultaneous monitoring and correlation of the visible chemiluminescent intensity and the mass spectrometric signal due to AlO* at m/e = 53 in a crossed beam or beam and "bottle" experiment involving Al$_2$ and O or Al and O$_3$. This might also be accomplished in a low-pressure flow tube experiment involving the same reactants, or TMA and atomic oxygen. Interference from the fragmentation of AlO$_2$, Al$_2$O$_2$, and other products at m/e = 53 could be avoided by appearance potential discrimination, or by inclusion of an inhomogeneous magnetic field in the mass spectrometric sampling train to preferentially detect the radical AlO species.[54] It would also be interesting to use a crossed beam experiment to look at the initial products from the reaction of TMA with O.

Also, flow tube experiments could be performed in an attempt to collisionally induce transitions between the proposed metastable states of AlO and the B state so that the fast AlO (B $\rightarrow$ X) emissions could be monitored. This is analogous to Broida's treatment of the BaO*-producing reactions,[34] and this may be the explanation for the observation of the AlO (B $\rightarrow$ X) transition in the laboratory oxidation of TMA by atomic oxygen,[3] which is not observed in lower pressure TMA atmospheric releases.

Finally, also analogous to BaO*, it seems likely that the reaction of Al atoms with N$_2$O will produce a chemiluminescence similar to that from Al + O$_3$.

31

SUMMARY

The suggestion is made that the chemiluminescent "continuum" associated with the oxidation of aluminum in a number of laboratory and upper atmospheric experiments may be attributed to emission from some combination of the $(A\ ^2\Pi)$ and lowest-lying $^4\Sigma^+$ and $^4\Pi$ states of AlO, and this seems to be consistent with the available experimental data. Pumping mechanisms based on the reaction of a loosely bound (1 to 3 eV) aluminum atom with atomic oxygen, or of atomic aluminum with a loosely bound oxygen atom, seem to explain reasonably the experiments analyzed.

Detailed analysis of the prototype reactions $Al_2 + O$ and $Al + O_3$ indicates that there are sound theoretical reasons to suspect that they will populate the $(A\ ^2\Pi)$, $^4\Pi$, and $^4\Sigma$ states efficiently in competition with the ground $(X\ ^2\Sigma^+)$ and excited $(B\ ^2\Sigma^+)$ states. Thus, pumping reactions of the type suggested may well produce AlO* in the suggested metastable states with a high quantum efficiency vis-a-vis the ground state without significantly populating the B state.

Previously suggested mechanisms for the aluminum/oxygen chemiluminescence do not appear compatible with the data presently available. In particular, the radiative recombination of AlO with O would have to proceed with an unreasonably large rate constant to explain the glow from either aluminum grenade or trimethylaluminum releases in the upper atmosphere.

REFERENCES

(1)   H.I. Schiff, "Kinetics of Atmospheric Gases," Final Report, Contract
        No. AF 19(628) 308, Upper Atmosphere Chemistry Group – McGill Univ.,
        Montreal, Canada (November 1965).

(2)   J. Pressman, A. Sharma, J. Padur, H.K. Brown and C. Rosen, "Upper
        Atmosphere Chemical Releases Study," Final Report, Contract No. NASW-
        985, GCA Corporation, Technology Division, Bedford, Massachusetts
        (August 1965).

(3)   M.J. Linevsky and F.N. Alyea, "Spectroscopy of Metal Oxides," Technical
        Report RADC-TR-73-391, General Electric Space Sciences Laboratory, King
        of Prussia, Pennsylvania (November 1973); and subsequent reports.

(4a)   M. Vanpee and T.F. Seamans, "Spectrophotometric Study of Premixed
        Trimethylaluminum–Oxygen Flames," Eleventh Symposium (International)
        on Combustion, The Combustion Institute (1967), pp. 931-938.

(4b)   M. Vanpee, E.C. Hinck and T.F. Seamans, "Characteristics of Premixed
        Trimethylaluminum–Oxygen Flames," Comb. Flame 9, 393-493 (1965).

(5)   A. Fontijn and P.H. Vree, "Chemiluminescent Gas-Phase Reactions Involving
        Electronically Excited Molecules, Trimethylaluminum and Diborane, Near
        3 mtorr," J. Phys. Chem. 70, 3377-3378 (1966).

(6)   J.L. Gole and R.N. Zare, "Determination of D_0^0 (AlO) from Crossed Beam
        Chemiluminescence of $Al + O_3$," J. Chem. Phys. 57, 5331-5335 (1972).

(7)   D.S.P. Wei, R.B. Hall and W.E. Maker, "Study of Laser-Supported
        Detonation Waves by Time Resolved Spectroscopy," J. Chem. Phys. 59,
        3692-3700 (1973).

(8)   T.H. Rautenberg, Jr., and P.D. Johnson, "Light Production in the Aluminum
        Oxygen Reaction," J. Opt. Soc. Am. 50, 602-606 (1960).

(9)   D.D. Woodbridge, "High Altitude Glow Measurements in Australia," Chemical
        Reactions in the Lower and Upper Atmosphere, Interscience Publishers,
        New York (1961), pp. 239-254.

(10)   N.W. Rosenberg, D. Golomb and E.F. Allen, Jr., "Chemiluminescent
        Techniques for Studying Nighttime Winds in the Upper Atmosphere,"
        J. Geophys. Res. 68, 3328-3330 (1963).

(11)   E.B. Armstrong, "Observations of Luminous Clouds Produced in the Upper
        Atmosphere by Exploding Grenades – III. Continuous Spectra from Night-
        time Glows," Planet. Space Sci. 11, 751-758 (1963).

33

REFERENCES (Cont.)

(12)   E.R. Johnson and C.H. Low, "Further Spectral Observations of Grenade
         Glow Clouds in the Lower Thermosphere," Aust. J. Phys. 20, 577-582 (1967).

(13)   E.R. Johnson, K.H. Lloyd, C.H. Low and L.M. Sheppard, "The Radiant
         Output of Grenade Glow Clouds in the Lower Thermosphere," Aust. J.
         Phys. 20, 683-695 (1967).

(14)   N.W. Rosenberg, D. Golumb and E.F. Allen, Jr., "Chemiluminescence of
         Trimethylaluminum into the Upper Atmosphere," J. Geophys. Res. 68,
         5895-5898 (1963).

(15)   D. Golomb and M.A. MacLeod, "Diffusion Coefficients in the Upper Atmosphere
         from Chemiluminous Trails," J. Geophys. Res. 71, 2299-2305 (1966).

(16)   E.R. Johnson and K.H. Lloyd, "Determination of Diffusion Coefficients from
         Observations on Grenade Glow Clouds," Aust. J. Phys. 16, 490-494 (1963).

(17)   K.H. Lloyd and L.M. Sheppard, 'Atmospheric Structure at 130-200 km
         Altitudes from Observations on Grenade Glow Cloud During 1962-1963,"
         Aust. J. Phys. 19, 323-342 (1966).

(18)   D. Golomb, O. Harang and F.P. DelGreco, "Upper Atmosphere Densities
         and Temperatures at 105-165 km from Diffusion and Spectral Intensity of
         AlO Trails," J. Geophys. Res. 72, 2365-2370 (1967).

(19)   D. Golomb, F.P. DelGreco, O. Harang, R.H. Johnson and M.A. MacLeod,
         "Neutral Diffusion Coefficients, Temperatures and Densities in the Lower
         Thermosphere," Space Research VIII (A.P. Mitru, L.G. Jacchia and
         W.S. Newman, Eds.), North Holland Publishing Co., Amsterdam (1968).

(20)   E.R. Johnson, "Twilight Resonance Radiation of AlO in the Upper Atmosphere,"
         J. Geophys. Res. 70, 1275-1277 (1965).

(21)   S.E. Johnson, G. Capelle and H.P. Broida, "Laser Excited Fluorescence
         and Radiative Lifetimes of AlO (B $^2\Sigma^+$ - X $^2\Sigma^+$)," J. Chem. Phys. 56
         663-665 (1972).

(22)   G.T. Best, D. Golomb, R.H. Johnson, D.F. Kitrosser, M.A. MacLeod,
         N.W. Rosenberg and W.K. Vichery, "Release of Diborane into the Upper
         Atmosphere," J. Geophys. Res. 76, 2187-2191 (1971).

(23)   L.G. Jacchia, "Revised Static Models of the Thermosphere and Exosphere
         with Empirical Temperature Profiles," Special Report 332, Smithsonian
         Astrophysical Observatory (Based on an Exospheric Temperature of 1000°K)
         (May 1971).

(24)   N.W. Rosenberg, D. Golomb and G.T. Best, "Notes on Aluminum Glows
         at High Altitudes," Air Force Cambridge Research Laboratories Memorandum
         (July 1971).

34

REFERENCES (Cont.)

(25)   F. Kaufman, "The Air Afterglow Revisited," Chemiluminescence and Bioluminescence (M.J. Cormier, D.M. Hercules and J. Lee, Eds.), Plenum Press, New York (1973), pp. 83-98.

(26)   C.T. Mortimer and P.W. Sellers, "Heats of Formation and Bond Energies — Part IX, Trimethylaluminum and Aluminum Triacetate," J. Chem. Soc. 1978-1981 (1963).

(27)   L.H. Long, "Dissociation Energies of Metal-Carbon Bonds and the Excitation Energies of Metal Atoms in Combination," Pure and Appl. Chem. 2, 61-69 (1961).

(28)   D.L. Hildenbrand, "Dissociation Energies of the Molecules AlO and Al_2O," Chem. Phys. Lett. 20, 127-129 (1973).

(29)   C.D. Jonah, R.N. Zare and Ch. Ottinger, "Crossed-Beam Chemiluminescence Studies of Some Group IIa Metal Oxides," J. Chem. Phys. 56, 263-274 (1972).

(30)   A. Schultz and R.N. Zare, "Comparison of $Ba + O_3$ and $Ba + N_2O$ Chemiluminescence," to be published.

(31)   W.S. Struve, J.R. Krenos, D.L. McFadden and D.R. Herschbach, "Chemiluminescence in Reactions of Halogen Atoms and Molecules with Alkali Dimers," Faraday Disc. Chem. Soc. 55 (1973).

(32)   M. Farber, R.D. Srivastava and O.M. Uy, "Mass Spectrometric Determination of the Heat of Formation of the AlO_2 Molecule," J. Chem. Phys. 55, 4142-4143 (1971).

(33)   J.L. Kinsey, "Molecular Beam Reactions," MTP International Review of Science, Phys. Chem. Ser. 1, Vol. 9, Chemical Kinetics (J.C. Polanyi, Ed.), University Park Press, Baltimore (1972), pp. 173-212.

(34)   C.R. Jones and H.P. Broida, "An Efficient Chemiluminescent Reaction," J. Chem. Phys. 59, 6677-6678 (1973); also C.R. Jones and H.P. Broida, "The Gas-Phase Reaction of Ba with N_2O - I." to be published.

(35)   R.W. Field, C.R. Jones and H.P. Broida, "The Gas-Phase Reaction of Ba with N_2O - II. Mechanism of Reaction," to be published.

(36)   H. Michels, United Aircraft Research Laboratories, private communication (1973)

(37)   J.K. McDonald and K.K. Innes, "A Low-Lying Excited Electronic State of the AlO Molecule and the Ground-State Dissociation Energy," J. Mol. Spectrosc. 32, 501-510 (1969).

(38)   D.S. Ginter, M.L. Ginter and K.K. Innes, "The Band Spectrum of the Al_2 Molecule," Astrophys. J. 139, 365-378 (1964).

(39)   W.A. Chupka, J. Berkowitz, C.F. Giese and M.G. Inghram, "Thermodynamic Studies of Some Gaseous Metallic Carbides," J. Phys. Chem. 62, 611-614 (1958).

35

REFERENCES (Cont.)

(40)   J. Drowart and R.E. Honig, "A Mass Spectrometric Method for the
         Determination of the Dissociation Energies of Diatomic Molecules,"
         J.Phys.Chem. 61, 980-985 (1957).

(41)   H.S. Hoffman, D. Golomb and G.T. Best, "Chemiluminescence of
         Na Vapor Released at Night," to be presented at the 55th Meeting of the
         American Geophysical Union, Washington, D.C. (April 1974).

(42)   D. Golomb and R.E. Good, "Clusters in Isentropically Expanding Nitric
         Oxide and Their Effect on the Chemiluminous NO-O Reaction," J.Chem.
         Phys. 49, 4176-4180 (1968).

(43)   R.J. Gordon, Y.T. Lee and D.R. Herschbach, "Supersonic Molecular
         Beams of Alkali Dimers," J.Chem.Phys. 54, 2393-2409 (1971).

(44)   G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic
         Molecules," Van Nostrand Reinhold Co., New York (1966).

(45)   See, for example, (a) D.R. Herschbach, "Reactive Scattering in Molecular
         Beams," Adv.Chem.Phys. 10, 319-393 (1966); and (b) D.R. Herschbach,
         "Transvibronic Reactions in Molecular Beams," Chemiluminescence and
         Bioluminescence (M.J. Cormier D.M. Hercules and J. Lee, Eds.),
         Plenum Press, New York (1973), pp. 29-41.

(46)   D.M. Lindsay, D.R. Herschbach and A.L. Kwiram, "ESR Spectra of Matrix
         Isolated CsO and RbO Molecules: $^2\Sigma$ Ground States and Inner Shell Bonding,"
         J.Chem.Phys. 60, 315-317 (1974).

(47)   K.D. Bayes and G.B. Kistiakowsky, "On the Mechanism of the Lewis-Rayleigh
         Nitrogen Afterglow," J.Chem.Phys. 32, 992-1000 (1960).

(48)   R.H. Oldenborg, J.L. Gole and R.N. Zare, "Chemiluminescent Spectra of
         Alkali-Halogen Reactions," J. Chem. Phys., in press.

(49)   J.D. Roberts and M.C. Caserio, Basic Principles of Organic Chemistry,
         W.A. Benjamin, Inc., New York (1964), pp. 343-344.

(50)   A.G. Davies and B.P. Roberts, "Peroxides of Elements Other than Carbon.
         Part XIV. The Mechanism of the Autoxidation of Organic Compounds of
         Lithium, Magnesium, Zinc, Cadmium and Aluminum," J.Chem.Soc. B,
         1074-1078 (1968).

(51a)   C.F. Cullis, A. Fish and R.T. Pollard, "The Slow Combustion of Aluminum
         Trimethyl," Proc.Roy. Soc. A 288, 123-132 (1965).

(51b)   C.F. Cullis, A. Fish and R.T. Pollard, "The Explosive Combustion of
         Aluminum Trimethyl," Proc.R.Soc. A 288, 413-423 (1965).

(52)   JANAF Thermochemical Tables, 2nd edition, U.S. Department of Commerce,
         National Bureau of Standards, Publication No. NSRDS-NBS 37 (June 1971).

36

REFERENCES (Cont.)

(53)   D. Golomb, Air Force Cambridge Research Laboratories, private
         communication.

(54)   M. Kaufman and C.E. Kolb, "Molecular Beam Analyzer for Identifying
         Transient Intermediates in Gaseous Reaction," Chem.Instr. 3, 175-189
         (1971).

37